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Seasonal variations of concentrations and optical properties of water soluble HULIS collected in urban environments

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Abstract. Major contributors to the organic aerosol include water-soluble macromolecular compounds (e.g. $HULIS_{WS}$: Water Soluble Humic LIke Substances). The nature and sources of $HULIS_{WS}$ are still largely unknown. This work is based on a monitoring in six different French cities performed during summer and winter seasons. $HULIS_{WS}$ analysis was performed with a selective method of extraction complemented by carbon quantification. UV spectroscopy was also applied for their chemical characterisation. $HULIS_{WS}$ carbon represent an important contribution to the organic aerosol mass in summer and winter, as it accounts for 12–22% of Organic Carbon and 34–40% of Water Soluble Organic Carbon. We found strong differences in the optical properties (specific absorbance at 250, 272, 280 nm and E2/E3 ratio) and therefore in the chemical structure between $HULIS_{WS}$ from samples of summer- and wintertime. These differences highlight different processes responsible for emissions and formation of $HULIS_{WS}$ according to the season, namely biomass burning in winter, and secondary processes in summer. Specific absorbance can also be considered as a rapid and useful indicator of the origin of $HULIS_{WS}$ in urban environment.

1 Introduction

The composition of the organic fraction of atmospheric aerosols and the respective contributions of primary and secondary sources are still poorly known, in part due to the considerable number of chemical species present in the particles. During the last years it was shown that HUmic LIke Substances (HULIS, i.e. polyacidic macromolecular species), are important contributors to the mass of the organic aerosol in rural, urban, marine, and biomass burning aerosol (Salma et al., 2007). The water soluble fraction of HULIS ($HULIS_{WS}$) most likely influences the hygroscopicity and the CCN ability of particles (Asa-Awuku et al., 2008; Dinar et al., 2006; Hatch et al., 2008; Salma et al., 2008) as well as their optical properties (Dinar et al., 2008). Currently, atmospheric HULIS research is hindered by the lack of a unified method for the analysis of these compounds and by a lack of knowledge on their sources (Graber and Rudich, 2006, and references therein). Recently, Feczko et al. (2007), showed a seasonal cycle of HULIS concentrations for six background sites, with one maximum in summer and/or one in winter. These variations have been seen as due to changes in either the sources of HULIS, or their formation processes, assuming that HULIS consist in a mixture of primary emissions and secondary products of various origins. In this paper, we investigate the temporal and structural variation of the $HULIS_{WS}$ fraction collected in urban environments.

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2 Experimental section

2.1 Sampling

Aerosol samples were collected in the urban background of 6 large French cities: Grenoble, Strasbourg, Lille, Paris, Toulouse, and Marseilles. Samples were collected on quartz fiber filters (150 mm diameter, Whatman, Q-MA) using DA-80 high volume samplers (DIGITEL), operating at $30\,m^3\,h^{-1}$. The filters were prepared before collection by firing them during 2 h at 600 °C. Sampling duration in

Marseilles was based on a day/night pattern, with 12 h sampling for a total period of 14 days during summer 2008. The sampling for all other locations took place daily once or twice a week, for periods of several months in summer 2008 and/or in winter 2008. Sampling periods and numbers of samples are reported in Table 1. More details about theses different campaigns can be found elsewhere (El Haddad et al., 2009; Pissot et al., 2010). Additional samples were collected in the small town of Chamonix, located in a valley of the French Alps (Aymoz et al., 2007). The sampling took place for a period of 10 days in winter 2007 (10 to 19 December 2007) in a suburban location. Sampling duration was based on a day/night pattern, with 12 h sampling. PM_{10} samples were collected on quartz fiber filters (Whatman®, 150 mm diameter) with a high-volume sampler (Tisch Andersen) at a flow rate of 30 $m^3\,h^{-1}$. More details about sampling can be found elsewhere (Baduel et al., 2009). Finally, some samples are coming from a tunnel study conducted in Marseilles in spring 2008. They were also collected with a similar protocol, except for a much shorter sampling time. After sampling, all filters were wrapped in aluminium foils, sealed in polyethylene bags and stored frozen until further analysis.

2.2 Analysis

These atmospheric samples are analyzed for EC/OC (Elemental and Organic Carbon), WSOC (Water Soluble Organic Carbon), and $HULIS_{WS}$ concentrations. EC/OC concentrations are determined by Thermo-Optical Transmission (TOT) method on a Sunset Lab analyzer (Aymoz et al., 2007). We are using the newly developed EUSAAR2 temperature program (Cavalli et al., 2010). It includes temperature steps up from 200 to 650 °C for the analysis of OC in 100% He, and up from 500 to 700 °C for the analysis of EC in 98% He+2% O_2. Automatic split time was always used for the distinction between EC and pyrolyzed OC. We analyzed fractions of 1.5 cm^2 of the filters, without any preparation.

For WSOC determination, 17–20 cm^2 of filter are extracted during 30 min in 12 mL of organic free water (Elgastat®). The surfaces extracted are adapted according to the OC concentrations measured in each sample. The extracts are filtered with Acrodisk filters (Pall Gellman®, 0.22 µm porosity) to remove any particles in suspension. WSOC is quantified with a TOC analyser (Shimadzu TOC-VCPH/CPN) by catalytic burning at 680 °C in oxygen followed by non dispersive infrared detection of the evolved CO_2.

The water soluble HULIS fraction is analyzed according to a protocol described in detail elsewhere (Baduel et al., 2009). Briefly, the water soluble fractions obtained from aerosol samples (see paragraph above) are passed through a weak anion exchange resin (GE Healthcare®, HiTrap™ DEAE FF, 0.7 cm ID × 2.5 cm length) without any pre-treatment. After this concentration step, the organic matter adsorbed is washed with 12 mL of a solution of NaOH 0.04 M (J. T. Baker®, pro analysis) to remove neutral components, hydrophobic bases, inorganic anion, mono- and di-acids initially retained in the resin. Finally, $HULIS_{WS}$ are quickly eluted in a single broad peak using 4 mL of a high ionic strength solution of NaCl 1 M (Normapur®). All flow rates are set at 1.0 mL min^{-1}. In this case, $HULIS_{WS}$ are operational defined as polyacidic compounds. UV-Vis absorption spectra are measured on-line after the extraction system, using a diode array detector (Dionex UV-VIS 340U), and recorded in the range 220–550 nm. The $HULIS_{WS}$ fraction is subsequently collected manually and the carbon content is analyzed with the same TOC analyser used for WSOC determination. Aliquots of the same filter extracts were analysed with Ionic Chromatography (IC) following the method described in Ricard et al. (2002). Cations (NH_4^+, K^+, Mg^{2+}, Ca^{2+}) were determined with a Dionex 100 IC, equipped with a CS12 column. Sodium could not be determined, due to high blank values coming from the filters quartz matrix. Inorganic anions (Cl^-, NO_3^-, SO_4^{2-}) and dicarboxylic acids (oxalate, glutarate, malonate, succinate and malate) were determined with a dionex DX500 equipped with an AS11 column.

3 Results and discussion

3.1 Atmospheric concentrations

The average concentrations and contributions of the $HULIS_{WS}$ fractions for all campaigns are presented in Table 1. The concurrent measurements of concentrations for OC, WSOC, and $HULIS_{WS}$ allow several observations. Figure 1 shows one year of $HULIS_{WS}$, OC and WSOC in Grenoble. $HULIS_{WS}$ follows the same seasonal trend as OC and WSOC, with a clear maximum in winter and minimum in summer. In summer, concentrations measured in Grenoble, Marseille and Toulouse are mostly between 0.2 and 1 µg C m^{-3} (average 0.63, 0.59 and 0.48 µg C m^3 respectively). In winter, in each site (Grenoble, Strasbourg; Lille, Chamonix and Paris), the spread in measured concentrations is higher, with values between 0.2 and 3 µg C m^{-3} (averages between 1.00 and 2.11 µg C m^3). The higher dispersion of the winter values, together with the very similar low values across the year might be due to dispersion phenomena, much more sensitive in winter when temperature inversion are most common.

Seasonal variations of $HULIS_{WS}$ in urban environments are relatively scarce to compare with. Limbeck et al. (2005) observed a similar seasonality in Vienna, Austria, with concentrations varying from ∼0.3 µg C m^{-3} in summer to ∼1.5 µg C m^{-3} in winter. Feczko et al. (2007) and Duarte et al. (2007) found a similar seasonal variation in Aveiro, Portugal, with concentrations varying from 0.3 to 0.9 µg C m^{-3} and from 0.6 to 2.33 µg C m^{-3} respectively between summer and winter. Krivácsy et al. (2008) also found similar seasonal variations in Auckland and Christchurch, New Zealand

Table 1. Variations of mean concentration of Water Soluble HULIS (in $\mu g\,C\,m^{-3}$) with standard deviation and its contribution to WSOC and OC aerosol fractions for each sample set.

Season	Location and sampling month	Number of samples	$HULIS_{WS}$ concentration ($\mu g\,C\,m^{-3}$)		$HULIS_{WS}$ contribution (%)	
			Average	min-max	WSOC	OC
Urban environment during cold season	Paris 08 (January to February)	16	1.08±0.86	0.34–2.25	34.1±9.0	14.6±3.2
	Lille 08 (January to February)	10	0.85±0.41	0.39–1.60	40.3±10.0	16.0±5.1
	Strasbourg 08 (January to February)	16	1.17±0.80	0.42–2.57	38.3±5.4	22.7±6.8
	Grenoble 08 (November to February)	69	1.38±0.71	0.20–3.12	39.5±7.6	16.4±6.1
Biomass burning background	Chamonix 07 (December)	16	1.47±0.95	0.37–4.36	23.4±3.1	12.7±1.8
Urban environment during summer	Marseilles 08 (July)	28	0.68±0.38	0.22–1.73	28.4±6.8	14.2±4.1
	Toulouse 08 (June to August)	18	0.51±0.30	0.11–1.48	42.7±10.8	17.3±5.0
	Grenoble 08 (May to August)	19	0.57±0.25	0.20–1.06	36.6±7.6	16.5±5.5
Mid season	Grenoble 08 (September to October)	13	0.62±0.28	0.31–1.27	30.6±6.5	14.9±5.6
	Grenoble 08 (March to April)	18	0.90±0.37	0.40–1.62	27.7±5.7	17.0±3.7

with concentrations varying from 0.35 to 2.11 $\mu g\,C\,m^{-3}$ and from 0.24 to 5.44 $\mu g\,C\,m^{-3}$ respectively between summer and winter.

The difference in winter enhancement observed between our and previous studies can be partly related to our selective extraction protocol. Indeed, we will show that our samples are strongly impacted by biomass burning emissions, and functionalized aromatic compounds (like phenol, vanillin, syringaldehyde, etc…) are consistently emitted by such sources (Graham et al., 2002). These compounds are associated with the HULIS fraction for the protocol used by Krivácsy et al. (2008), according to Limbeck et al. (2005), and for the protocol used by Duarte et al. (2007), according to Sullivan and Weber (2006) while they are excluded from it in our protocol (Baduel et al., 2009).

Second, the contribution of $HULIS_{WS}$ to WSOC as measured in our study is between 28–43% and the contribution to OC is in the range 14–22%, stressing the strong contribution of $HULIS_{WS}$ to the organic aerosol mass all year long. The $HULIS_{WS}$ contributions in our study are comparable to data obtained with a comparable extraction method for polluted rural background: 24–44% of WSOC for a yearly study (Decesari et al., 2001).

Finally, rather large concentrations of $HULIS_{WS}$ are measured in vehicle emissions as compared to $HULIS_{WS}$ concentrations found in urban background in summer. However, in the former case $HULIS_{WS}$ only represent a relatively small fraction of OC due to the important hydrophobic character of freshly emitted organic aerosol in vehicle exhaust (El Haddad et al., 2009).

3.2 Chemical characterisation

Just as Humic substances, HULIS consist of poly-conjugated structural elements carrying carboxyl, hydroxyl and carbonyl polar groups (Decesari et al., 2001; Duarte et al., 2008, 2007; Graham et al., 2002; Kiss et al., 2002; Tagliavini et al., 2006). It is largely demonstrated that HULIS present light absorption in the UV-Vis range (Graber and Rudich, 2006). Although the spectra are essentially featureless, with a sharp decrease between 200 and 400 nm, clear shoulders can be seen for HULIS as for fulvic acids in the wavelength region between 250 and 300 nm. This absorption, characteristic of fulvic acids is generally attributed to $\pi - \pi^*$ electron transitions in moieties containing C=C and C=O double bonds (Chin et al., 1994; Peuravuori and Pihlaja, 1997).

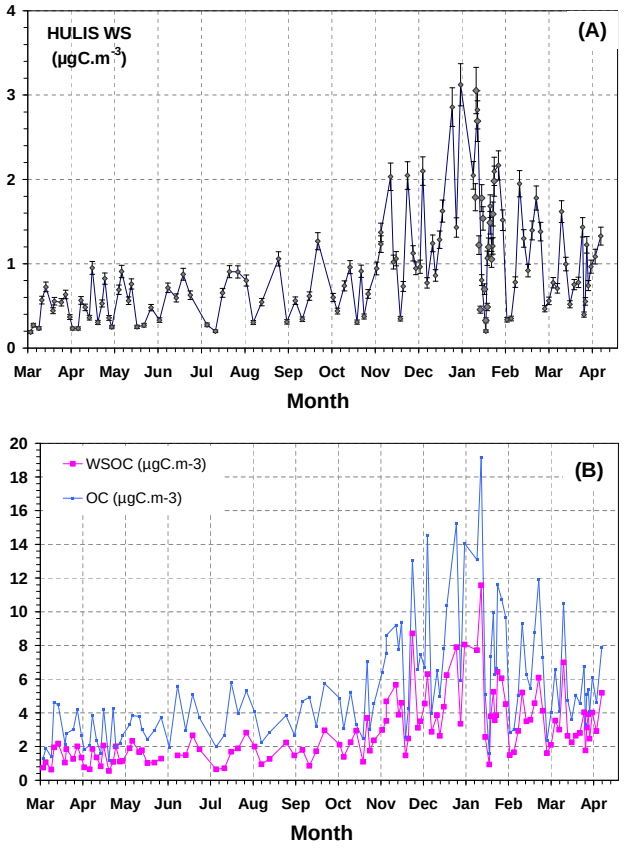

Fig. 1. Seasonal evolution of $HULIS_{WS}$ **(A)**, OC and WSOC **(B)** concentrations (µgC m^{-3}) in Grenoble.

Following this, many studies on aquatic humic substances have found large correlations between aromaticity and absorbance at various wavelengths (254, 272 and 280 nm), as for example in Hautala et al. (2000). In particular, absorption between 270 and 280 nm is often used to represent aromaticity in humic substances because $\pi - \pi^*$ electronic transitions of polyenes, benzoic acids, PAHs (with a minimum of 2 to 3 cycles) and aniline derivatives occur in this region and are recurrent structural patterns in humic substances (Chin et al., 1994; Traina et al., 1990). These same structures (except PAHs) have been identified by ^{13}C-NMR in $HULIS_{WS}$ (Sannigrahi et al., 2006). Another indicator of aromaticity widely used in aquatic humic substances research (Li et al., 2009; Peuravuori and Pihlaja, 1997), and previously applied on $HULIS_{WS}$ (Duarte et al., 2005; Krivácsy et al., 2008) is the ratio (E2/E3) of absorbance at 250 nm over absorbance at 340 nm, which is strongly correlated with total aromaticity in humic substances and does not depend on carbon measurements. We will thus discuss our spectroscopic measurements (mainly specific absorbance at 254 nm) in terms of relative aromaticity in $HULIS_{WS}$ for our different sites and seasons. These are summarized in Table 2.

First, one can see that for the overall sample set obtained in Grenoble in 2008 (the only one covering all seasons), we can observe three different trends, corresponding to samples collected in summer, winter, and mid seasons, respectively. High (respectively low) specific absorbance during the cold (respectively warm) season lead to high (respectively low) slope for the regressions between concentrations and absorbance, with results from mid seasons in-between. Correlations for the regression lines are excellent ($r^2 > 0.8$) and values of the average specific absorbance for each season are statistically different, indicating a consistent pattern over each of the data sets. Further, the intercepts are low in each case, an indication that our extraction protocol is efficient in getting rid of any inorganic species absorbing at 250 nm. Second, the Table 2 indicates that all other sample sets follow a similar pattern, with large specific absorbance in the cold season and a much lower one in summer, irrespective of the sampling locations. For each site in summer and winter, regressions between absorbance at any wavelength and concentrations also present excellent correlation coefficients ($r^2 > 0.8$), with essentially no difference in correlation coefficients between various sites. Mid season data in Grenoble show a lesser correlation (r^2 between 0.39 and 0.79 depending on wavelength), that might be related with continuous shifts between summer and winter like conditions and sources during the midseason.

3.3 Characteristics of the combined data sets

In a second step, samples from the different sites are gathered according to the sampling season and the associated regression lines are plotted in Fig. 3. It shows that the correlations between the concentrations of $HULIS_{WS}$ and its absorbance at 250 nm are strongly different between the summer ($n = 65$) and winter ($n = 73$) sample sets. This agrees well with different chemical structures for winter and summertime $HULIS_{WS}$, which can be related to seasonal differences in emissions and/or formation processes. Moreover, the excellent correlation for each regression shows the stability of the bulk structure of the $HULIS_{WS}$ extracted during these two different periods, with a very low dependency on the specific site.

3.3.1 Winter

$HULIS_{WS}$ collected in winter present a strong absorbance at the wavelength of 250, 272 and 280 nm, as well as a smaller E2/E3 ratio, which might be attributed to an important contribution of aromatic structures (Fig. 2). As mentioned above, it is known that biomass combustion processes release aromatic species at high concentration into the atmosphere (Graham et al., 2002). It is proposed that such combustions represent the most probable source of $HULIS_{WS}$ in urban areas during the burning season (Krivácsy et al., 2008). This is further supported by the correlations between HULIS and

Table 2. Correlations between TOC (x, µgC) and absorbance data at various wavelength (y, AU) for different sample sets from urban environments in summertime and/or in wintertime. In parenthesis is the correlation coefficient. The specific absorbance ε ($cm^2\ mg_C^{-1}$) is the average value of the whole sample set for each described site. Uncertainties include standard deviation of the sample set.

Season	Location and sampling month	Number of samples	250 nm	272 nm	280 nm	300 nm	E2/E3
Urban environment during cold season	Paris (January to February)	16	y=41.0x−0.5 (r^2=0.99) ε=40.9±3.2	y=28.0+1.15 (r^2=0.99) ε=29.45±3.0	y=25.9x+1.3 (r^2=0.99) ε=28.0±2.1	y=22.83x+0.18 (r^2=0.99) ε =2=3.4±2.01	3.23±0.18
	Lille (January to February)	10	y=41.5x−0.1 (r^2=0.92) ε=41.5±6.4	y=33.9x−2.5 (r^2=0.95) ε=30.1±4.72	y=30.4x−2.15 (r^2=0.92) ε=27.3±4.1	y=24.8x-0.1 (r^2=0.89) ε=22.9±3.8	3.47±0.23
	Strasbourg (December to February)	16	y=41.3x−0.7 (r^2=0.98) ε=40.5±4.8	y=28.1x−0.7 (r^2=0.96) ε=27.7±3.8	y=27.9x+0.01 (r^2=0.98) ε=26.3±4.2	y=22.5x−0.1 (r^2=0.96) ε=21.7±3.6	3.29±0.22
	Grenoble (November to February)	9	y=45.9x+3.1 (r^2=0.94) ε=49.3±5.9	y=35.9x+0.6 (r^2=0.93) ε=36.7±4.4	y=32.4x+2.1 (r^2=0.96) ε=34.5±3.4	y=27.3x+1.9 (r^2=0.93) ε=29.4±3.6	3.14±0.20
Biomass burning background	Chamonix (December)	16	y=58.1x+0.8 (r^2=0.98) ε=58.9±6.5	y=39.9x+0.7 (r^2=0.98) ε=41.6±4.1	y=34.07x+2.0 (r^2=0.98) ε=36.7±4.1	y=32.8x−0.7 (r^2=0.98) ε=32.4±3.2	2.88±0.18
Urban environment during summer	Marseilles (July)	28	y=19.1x+1.6 (r^2=0.92) ε=22.5±3.7	y=13.7x+0.13 (r^2=0.91) ε=14.1±2.3	y=12.4x+0.1 (r^2=0.91) ε=12.7±2.1	y=10.8x (r^2=0.92) ε=10.8±1.8	5.90±0.85
	Toulouse (June to August)	18	y=15.4x+2.5 (r^2=0.88) ε=21.6±4.7	y=13.2x+2.3 (r^2=0.94) ε=18.8±2.4	y=12.9x+1.8 (r^2=0.94) ε=17.2±2.4	y=9.8x+1.76 (r^2=0.85) ε=14.3±3.0	4.59±0.33
	Grenoble (May to August)	19	y=19.9x+1.6 (r^2=0.84) ε=22.8±4.7	y=15.3x+0.9 (r^2=0.83) ε=17.3±3.6	y=14.5x+1.4 (r^2=0.84) ε=16.9±2.8	y=12.9x+0.9 (r^2=0.87) ε=14.6±3.1	4.55±0.33
Mid season	Grenoble (Septtember to October)	13	y=36.9+1.3 (r^2=0.79) ε=39.14±9.8	y=28.5x+0.6 (r^2=0.78) ε=29.5±7.4	y=24.4x+2.8 (r^2=0.69) ε=27.1±6.4	y=13.9x+4.3 (r^2=0.39) ε=22.8±12.9	3.59±0.31
	Grenoble (March to April)	41	y=26.9x+6.1 (r^2=0.54) ε=38.1±9.9	y=20.83x+4.52 (r^2=0.62) ε=29±7.5	y=21.9x+3.3 (r^2=0.60) ε=28.1±7.2	y=16.3x+3.6 (r^2=0.67) ε=23.1±6.3	3.35±0.32

biomass burning tracers such as levoglucosan, dehydroabietic acid, and fine potassium (Feczko et al., 2007; Krivácsy et al., 2008; Mayol-Bracero et al., 2002). These results are also in good agreement with recent chemical characterisation studies of WSOC from biomass burning source (Duarte et al., 2008; Decesari et al., 2007). A primary mode of HULIS formation could derive from the incomplete breakdown of polymeric carbohydrates and lignin which can be further modified in the process of combustion. HULIS formation can also be secondary in nature, resulting from the transformation of pyrogenic semi-volatile organic compounds through condensation reactions with other molecules (Mayol-Bracero et al., 2002). Hoffer et al. (2004) and Gelencsér et al. (2003) also showed that HULIS may be produced in cloud droplets from aromatic acid precursors which may originate from biomass burning. Finally, Decesari et al. (2002) proposed that HULIS can derive from the reaction of soot particles with atmospheric oxidants. In this case, reactions with ozone can lead to the degradation of aromatic structures and to the formation of carbonyl and carboxyl functional groups (Bloss et al., 2005).

K^+_{ndust} is considered a reliable tracer for biomass burning (Pio et al., 2008), but must be cautiously evaluated as K^+ also has terrestrial and marine sources. In Grenoble and Chamonix, we considered the marine source as negligible and evaluated the terrestrial contribution from the measured Ca^{2+} concentrations by applying to them an average

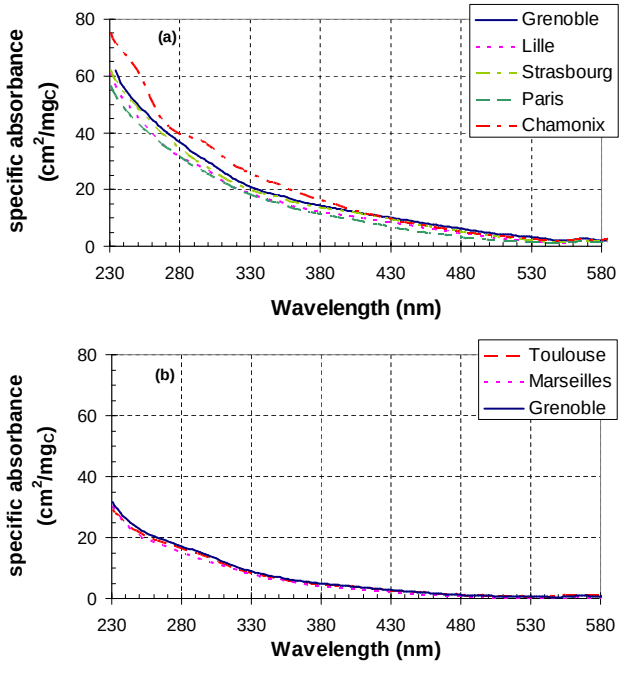

Fig. 2. Typical absorption spectra for $HULIS_{WS}$ for each city. **(a)** Winter cities, **(b)** summer cities.

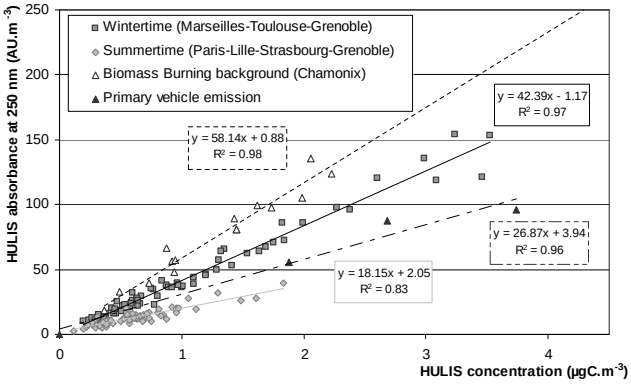

Fig. 3. Correlations between HULIS carbon concentration ($\mu gC\,m^{-3}$) and UV HULIS absorbance at 250 nm (Arbitrary Unit per cube meter). Atmospheric HULIS data coming from different French cities are gathered by seasons. HULIS coming from Chamonix (biomass burning background) are not mix with other winter sample set.

$(K^+/Ca^{2+})_{dust}$ ratio. This average ratio was estimated from a linear regression of the summer's ion concentrations in Grenoble. The observed correlation ($r^2 = 0.58$, 20 points) yields $(K^+/Ca^{2+})_{dust} = 0.11$; this value is close to 0.12 the value adopted by Puxbaum et al. (2007) based on measured concentrations from summer aerosol at three European continental sites in summer. In Strasbourg and Paris, we applied the same $(K^+/Ca^{2+})_{dust} = 0.11$, resulting in a correction that did not exceed 14% in Strasbourg and reached up to 50% (average 28%) in Paris. Lille could not be corrected in the same way, as potassium also has a marine source that would have to be accounted for, which was not possible due to the very high blank values for sodium on the quartz filter (see Sect. 2.2). The observed correlations between estimated K^+_{ndust} and $HULIS_{WS}$ are summarized in Table 3. They are very clear for all 4 cities. Moreover, for Paris, Strasbourg and Lille, independent measurements of Levoglucosan, another tracer for biomass burning, also show very clear correlations between $HULIS_{WS}$ and the tracer (Pissot et al., 2010). Such correlations do not necessarily mean common sources, especially in winter, when temperature inversions are common and can induce co-varying concentrations of any sources blocked under the inversion. In order to exclude this hypothesis, we looked into the correlation between $HULIS_{WS}$ and EC, as a representative primary urban emission. EC and $HULIS_{WS}$ are not related (Table 3), thus excluding a meteorologically induced correlation between K^+_{ndust} and $HULIS_{WS}$, and indicating different sources for EC and $HULIS_{WS}$. EC is produced by combustion sources, which in urban settings in winter are mainly fossil fuel combustion and biomass burning in the form of residential wood burning. It has been shown in Göteborg (Szidat et al., 2009) and Zurich (Szidat et al., 2006) that fossil fuel combustion contribute for 75 to 90% of EC, leaving biomass burning as a minor source for EC. The non correlation of $HULIS_{WS}$ with EC, together with the clear correlation observed with K^+_{ndust} thus indicates that wood combustion is probably the main source of $HULIS_{WS}$ in the large French cities studied during winter. In the mid seasons in Grenoble, the correlation between $HULIS_{WS}$ and K^+_{ndust} gets weaker ($r^2 = 0.49$) although with a very similar slope (4.57). In the same time, the correlation with EC completely disappears ($r^2 = 0.05$). This agrees with a shift between summer and winter sources.

Yet, $HULIS_{WS}$ collected in Chamonix present a stronger absorbance than those collected in winter in other cities (Table 2 and Fig. 3) while we know that a very large fraction of the PM at this site is due to local emissions of wood combustion from domestic heating (Marchand et al., 2004). Measurements of NO and O_3 near the sampling site are available from the local Air Quality Monitoring Network, and indicate average values of 116 ± 93 and $4\pm2\,\mu g\,m^{-3}$ respectively. This is a typical situation where O_3 is titrated by local traffic emissions of NO, under very stagnant conditions in a deep Alpine valley: Chamonix lies at 1500 m a.s.l., surrounded by mountains up to 4800 m (Mont Blanc). The same data are available in the other cities, and the situation is nowhere as dramatic as in Chamonix with typical concentrations for ozone around 20–50 $\mu g\,m^{-3}$, indicating a much less stagnant situation on average. This would mean that the Chamonix aerosol can be regarded as unaffected yet by ozone chemical ageing. As reaction with ozone tends to destroy double bonds, it would reduce the specific absorbance of $HULIS_{WS}$ and their E2/E3 ratio, which would agree with our observation of a higher specific absorbance at 250 nm and higher E2/E3 ratio for $HULIS_{WS}$ in Chamonix as compared to other French cities. Further investigations on this point are in progress, with direct measurements of $HULIS_{WS}$ fractions and characteristics from samples collected at the emission from different sources of biomass burning.

3.3.2 Summer

Summer $HULIS_{WS}$ present a lower specific absorbance at all wavelength and a higher E2/E3 ratio, an indication of a more pronounced aliphatic character (Fig. 2). Such structures may belong to secondary products from some biogenic or anthropogenic sources. Decesari et al. (2007) suggested secondary atmospheric oxidation processes as possible sources for atmospheric WSOC in an urban area in summer. This last study also showed that the composition of biogenic and anthropogenic secondary organic aerosol (SOA) are characterized by a high content of aliphatic structures (high H-C and H-C-O content) and a systematic low aromatic content. Recent studies using ^{1}H-NMR have shown that prolonged ageing of SOA leads to a reduction of hydroxyl and aromatic groups (Moretti et al., 2008). Numerous investigations have confirmed the existence of polymeric/oligomeric compounds with molecular masses up to 1600 Da in various SOA formed from photooxidation of both anthropogenic (Gross et

Table 3. Correlations observed in winter between $HULIS_{WS}$ (y; µg C m^{-3}) and K^+_{ndust} (x; µg m^{-3}), and between $HULIS_{WS}$ (y; µg C m^{-3}) and EC (x; µg C m^{-3}).

Location and sampling month	Number of samples	K^+_{ndust}	EC
Paris 08 January to March	16	$y = 15x - 0.12$ (r^2=0.74)	$y = 1.62x - 0.03$ (r^2=0.26)
Strasbourg 08 January to March	16	$y = 6x + 0.11$ (r^2=0.81)	$y = 3.35x + 0.22$ (r^2=0.34)
Grenoble 08 January to March	9	$y = 5.5x + 0.34$ (r^2=0.87)	$y = 0.38x + 0.59$ (r^2=0.49)
Chamonix 07 December	16	$y = 4.3x + 0.23$ (r^2=0.77)	$y = 0.14x + 0.71$ (r^2=0.40)

al., 2006; Wyche et al., 2009) and biogenic (Surratt et al., 2006; Tolocka et al., 2004) precursors in simulation chamber studies. Such polymeric products present spectral properties similar to HULIS in atmospheric aerosols (Limbeck et al., 2003), despite the fact that the majority of HULIS compounds seem to be in the range of 400–700 Da (Graber and Rudich, 2006). During warmer periods in urban site, maximum molecular weight of the HULIS determined with Size Exclusion Chromatography coupled to UV detection had shown positive correlations with temperature and ozone. Theses results suggest photochemical processes as a source of secondary HULIS (Samburova et al., 2005). Soot oxidation by ozone has also been suggested as a secondary source of HULIS (Decesari et al., 2002), where aromatic structures are degraded, leading to the formation of carbonyl and carboxylic functional groups (Bloss et al., 2005). Such oxidation processes leading to HULIS by aerosol ageing can also be initiated by OH and NO_3 radicals, or by soluble oxidants such as H_2O_2, organic peracids and organic peroxides (Jammoul et al., 2008; Vione et al., 2006). As a consequence, in urban environments, HULIS can both be secondarily formed by chemical reactions from various precursors and directly emitted into the atmosphere by fossil fuel combustion. Our data show that ambient $HULIS_{WS}$ in summer exhibit a lower specific absorbance than $HULIS_{WS}$ representative of the primary automobile emission source. This could be viewed as a mixing process between this primary source and secondarily produced $HULIS_{WS}$ exhibiting a much lower specific absorbance. Correlation between EC and $HULIS_{WS}$ (Table 3) is very poor in summer, which indicates that fossil fuel combustion is actually not an influential source of $HULIS_{WS}$ in summer. On the opposite, we found very good correlations between oxalic acid and $HULIS_{WS}$ in summer on all our sites (Table 3). Although the sources of oxalic acid are not extremely well known, especially in urban environments, it is thought to be mainly secondary (Legrand et al., 2007, and references therein) and we thus see the observed correlation as an indication of the probable secondary origin of $HULIS_{WS}$ in our urban sampling sites. Together with the observation that the measured urban $HULIS_{WS}$ in summer have a lower absorbance than those measured in our tunnel experiment, this would indicate that the secondarily formed $HULIS_{WS}$ have indeed the lowest specific absorbance, which would indicate mainly a low aromaticity content. This would agree with the mechanism invoked for pyruvic acid photoinduced oligomerization, that mainly forms aliphatic polymeric structures (Guzman et al., 2006).

3.3.3 SRFA and use of specific absorbance

Suwannee River Fulvic Acid (SRFA) (IHSS, 15101F) is mainly used in the literature as a model compound for atmospheric $HULIS_{WS}$ for different types of experiments (Baduel et al., 2009). However, it is hypothesized that $HULIS_{WS}$ show structural differences with aquatic humic substances, like a higher aliphatic structure and a lower degree of oxidation (Graber and Rudich, 2006). A data set for SRFA was obtained in our study for measurements on the same standard solution, for a range of carbon masses between 0 and 20 µg. Figure 4 indicates that this standard compound presents a specific absorbance at 250 nm close to that of the samples collected in urban areas in winter, with a slightly lower value compared to that obtained for the data set from the Alpine valley in Chamonix. Conversely, characteristics of $HULIS_{WS}$ collected in summer may largely differ from that of SRFA, with a much lower absorbance at 250 nm for the former. Therefore, it is not appropriate to consider SRFA as a representative standard for the whole $HULIS_{WS}$ fraction. Absolute calibration of UV absorbance with SRFA can not be used for quantification of $HULIS_{WS}$ because it can overestimate the carbon content of HULIS by a factor of 3.

Table 4. Correlations observed in summer between $HULIS_{WS}$ (y; $\mu g\,C\,m^{-3}$) and oxalic acid (x; $\mu g\,m^{-3}$), and between $HULIS_{WS}$ (y; $\mu g\,C\,m^{-3}$) and EC (x; $\mu g\,m^{-3}$).

Location and sampling month	Number of samples	Oxalic acid	EC
Marseilles 08 July	16	$y = 5.4x + 0.20$ (r^2=0.77)	$y = 0.35x - 0.10$ (r^2=0.48)
Toulouse 08 June to August	10	$y = 4.2x - 0.10$ (r^2=0.72)	$y = 0.22x + 0.26$ (r^2=0.18)
Grenoble 08 May to August	16	$y = 4.2x + 0.23$ (r^2=0.72)	$y = 0.40x + 0.08$ (r^2=0.38)

However, UV absorption could be a useful and rapid indicator of the origin of $HULIS_{WS}$ in atmospheric samples. Figure 4 presents specific absorbance in our samples as a function of the time of year. Average values of 22.6±4.5 in summer and 42.3±6.0 in winter were observed. Relative standard deviation represent about 15–20% in summer and 10–15% in winter, much lower than the relative seasonal variation. We can conclude that this measurement is useful to give a good idea of the formation processes of the $HULIS_{WS}$ fractions.

The seasonal cycle for specific absorbance of $HULIS_{WS}$ has only been observed in Grenoble. Yet, because the sources inferred in summer (secondary production) and in winter (residential wood burning) in each subset of cities (Lille, Strasbourg, Grenoble, Paris and Chamonix in winter; Grenoble, Toulouse and Marseille in summer) are very seasonal and ubiquitous, we argue that the seasonal cycle observed in Grenoble is most probably valid in the other cities as well.

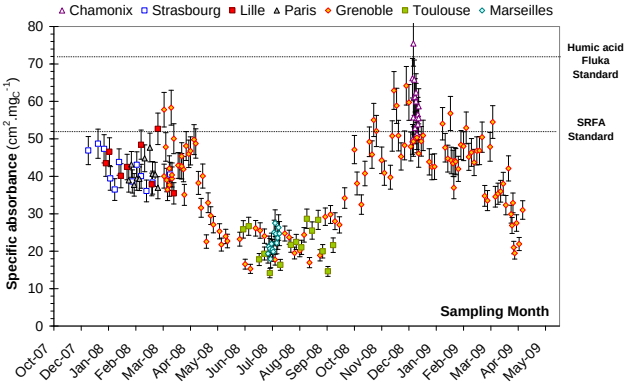

Fig. 4. Specific absorbance at 250 nm of HULIS from atmospheric aerosol samples depending on sampling season and environment. Also shown are the specific absorbance at the same wavelength for two popular reference Fulvic and Humic acids.

4 Conclusions

Organic aerosol concentrations have been monitored in six different French cities during winter and summer. Water-soluble HULIS comprises about 23–43% of WSOC and 13–23% of OC in different urban environments. The HULIS contribution is significant indicating the global importance of HULIS in controlling the mass concentration of organic aerosol.

Specific absorbance at 250, 272, 280 and 300 nm was used to investigate structural differences in $HULIS_{WS}$ as a function of sampling site and season. Specific absorbance does not significantly change from one city to another for a given time period, but depends strongly on the season. The only exception is Chamonix in winter, wher $HULIS_{WS}$ present a higher specific absorbance compared to other cities. This is tentatively attributed to suppressed ageing because of ozone titration by NO in stagnant air of a deep alpine valley, leading us to argue that ageing causes a decrease of specific absorbance for $HULIS_{WS}$. Summer $HULIS_{WS}$ exhibit a lower specific absorbance, characteristic of more aliphatic/less aromatic structures. Those seasonal differences are more significant than any intra-seasonnal or geographic variability, which points to formation processes or sources largely independent of the local emissions. Indeed, strong correlations with K^+_{ndust} in winter suggest residential wood burning as the main source for $HULIS_{WS}$ in winter; and strong correlations with oxalic acid in summer points towards secondary production as the probable source of $HULIS_{WS}$ in summer. As these sources are ubiquitous, we hypothesize that although it has strictly been observed only in Grenoble, the seasonal cycle in specific absorbance, driven by a source change from wood burning in winter to secondary production in summer, is a common feature of most urban environments.

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